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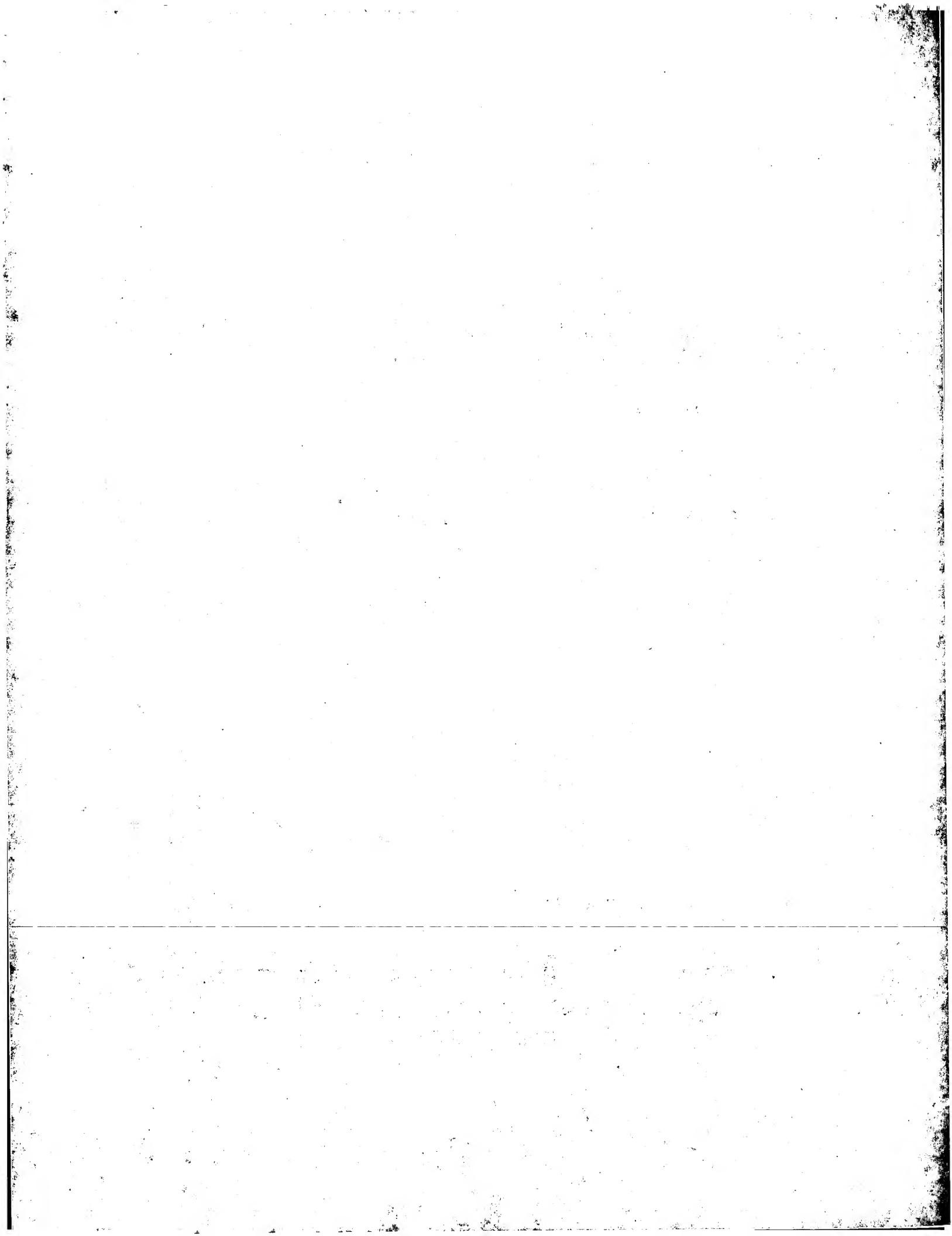
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## (54) Amylose granule and its preparation

(57) Novel amylose granules advantageously used in the fields of food products, pharmaceuticals and cosmetics exist in an approximately globular-shape of amylose granule or in a conjugation form consisting of two or more of the amylos granules linked together, and having about 2-10 µm in diameter or major axis, B type form of starch on powder X-ray diffraction analysis, the number-average molecular weight of about 4,000-7,000 on gel permeation chromatography, and the weight-average molecular weight per the number-average molecular weight of about 1.4-1.7.

The granules may be prepared by allowing cyclomaltoextrin glucanotransferase (EC 2.4.1.19) to act on an aqueous solution containing a cyclodextrin or starch. In examples the enzyme is derived from *Bacillus stearothermophilus* or *Bacillus macerans*; other sources are mentioned.

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FIG. 1

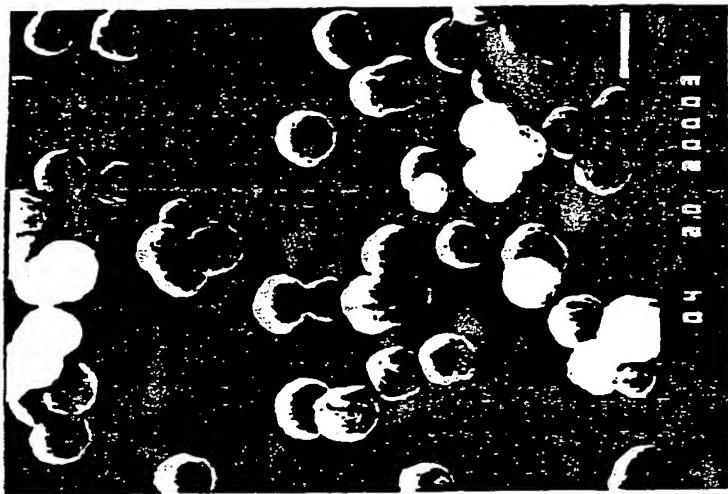


FIG. 2

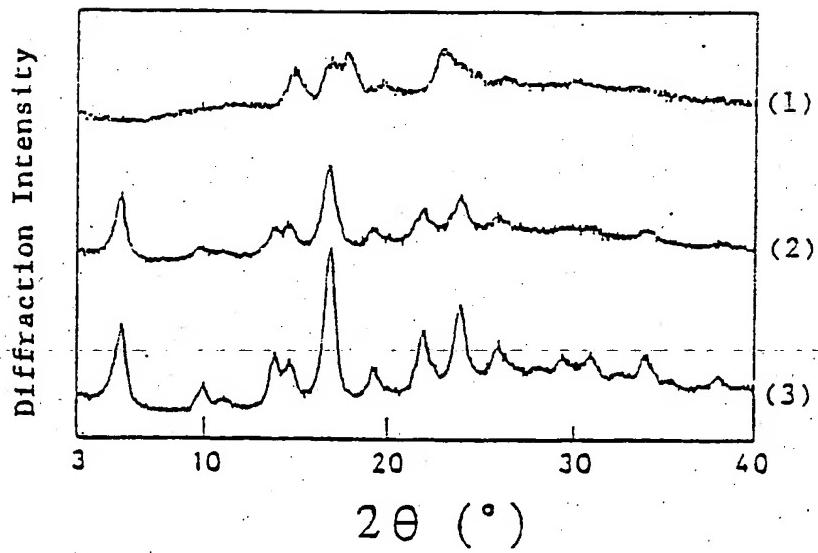
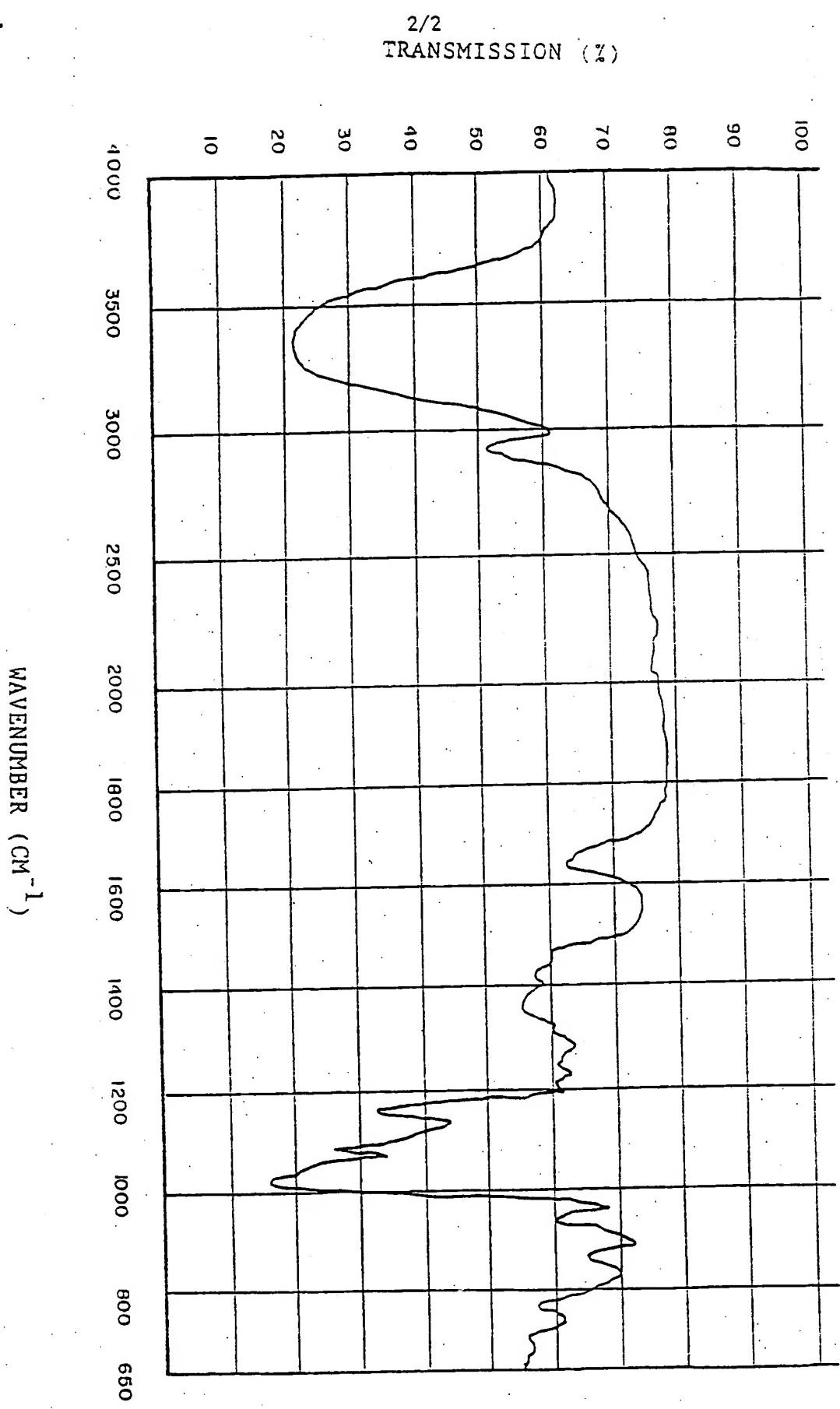


FIG. 3



## AMYLOSE GRANULE AND ITS PREPARATION

The present invention relates to an amylose granule and its preparation, more particularly, it relates to an amylose granule having a specific form, X-ray diffraction pattern, and molecular weight; and to a process which comprises allowing cyclomaltodextrin glucanotransferase to act on an aqueous solution containing a cyclodextrin or starch to form an amylose granule which is insoluble in the aqueous solution, and recovering the resultant amylose granule.

Conventional methods for preparing amylose are as follows:

- (1) The complex precipitation method using butanol reported by T. J. Schoch, Journal of American Chemical Society, Vol. 64, p.2957-2961 (1942);
- (2) The extraction method using hot water reported by K. H. Meyer, Helvetica Chimica Acta, Vol. 24, p.378-389 (1941);
- (3) The salting-out method using magnesium sulfate disclosed in Bus et al., Japanese Patent Publication No.8,675/57 and United States Patent Nos.2,822,305 and 2,829,990;

- (4) The hydrolysis method using debranching enzymes such as pullulanase and isoamylase disclosed in Sugimoto et al., Japanese Patent Publication No.21,420/79; and
- (5) The saccharide-transferring reaction method using cyclomaltodextrin glucanotransferase which transfers a saccharide to its acceptor reported by Hans Bender, Carbohydrate Research, Vol.65, pp.85-97 (1978).

The methods for preparing amylose (1), (2) and (3), however, have some drawbacks: The yield of amylose is usually lower than 25 w/w % against the material starch; the quality and yield of amylose dependently vary on the type and lot number of the material starch; and there is also a possibility of a contamination of amylopectin into amylose.

Although, the yield of amylose in the method (4) is relatively high, i.e. 80 w/w % or higher, against the material starch, the method only provides a mixture of long- and short-chain length of amyloses which usually require complicated separation processes. Furthermore, there is a possibility of a contamination of intact starch which has not been hydrolyzed by a starch-debranching enzyme.

The concentration of the amylose prepared by the method (5) is relatively low, and the yield of amylose is relatively low, i.e. lower than 30 w/w %, in spite of a requirement of an organic precipitant such as methanol.

It has been a strong demand to overcome the drawbacks in conventional methods for preparing amylose, and to establish a relatively high-quality of amylose granule with a relatively uniform molecular-weight, as well as to a preparation which stably facilitates the formation of a relatively high-quality of amylose granule in a relatively high-yield.

The present invention aims to overcome the above drawbacks, more particularly, the present inventors studied novel amylose granule and its preparation using cyclomaltodextrin glucanotransferase (EC 2.4.1.19).

As a result, the present inventors found that novel amylose granule was obtained by allowing cyclomaltodextrin glucanotransferase (hereinafter abbreviated as "CGT-ase") to act at a relatively low-temperature on an aqueous solution containing a relatively high-concentration of a cyclodextrin or starch to form and precipitate an amylose granule in the aqueous solution, and found that a relatively high-quality of amylose granule was readily obtained in a relatively high-yield by recovering the amylose granule.

Thus, the present inventors had accomplished the present invention.

Furthermore, the present inventors found that the present invention has the following advantageous features:

- (1) Since an insoluble amylose granule is formed and precipitated in a reaction solution, the separation and recovery of the amylose granule is not difficult and a relatively expensive organic-precipitant such as methanol and butanol is not required;
- (2) The yield of the amylose granule is readily increased to a 50 w/w % or higher against the material;
- (3) The molecular weight of amylose granule is controllable by varying the material starch, origin of CGT-ase, and the conditions such as the amount of CGT-ase and the reaction time and temperature.

The present invention will now be described in more detail by way of example only with reference to the drawings in which:

FIG.1 shows an electron microscopic photograph (x 2,000) of an example of the amylose granules according to the present invention.

FIG.2 shows the powder X-ray diffraction patterns of starch specimens and the amylose granules according to the present invention, i.e. the patterns (1), (2) and (3) are A type form of starch (corn starch), B type form of starch (potato starch), and the X-ray diffraction pattern of the amylose granules.

FIG.3 shows the infrared absorption spectrum of an example of the amylose granules according to the present invention.

The material cyclodextrins usable in the invention include one or more of  $\alpha$ -cyclodextrin,  $\beta$ -cyclodextrin and  $\gamma$ -cyclodextrin. Furthermore, commercialized cyclodextrins and those prepared by allowing CGT-ase to act on starch can be favorably employed. When a cyclodextrin contains a concomitant such as glucose and relatively-low molecular weight of oligosaccharides, it is recommendable to remove such concomitant as much as possible prior to its use.

Furthermore, it can be advantageously carried out to form cyclodextrins by allowing CGT-ase together with a starch-debranching enzyme to act on starch to form cyclodextrins and amylose granules.

The starch sources usable in the invention include a subterranean stem starch, for example, potato starch, cane starch and tapioca starch; and a terrestrial stem starch, for example, corn starch, wheat starch and rice starch. The methods for allowing CGT-ase to act on the material starch in the invention include those which comprising adding CGT-ase to

a starch slurry, and heating the resultant mixture to effect the gelatinization and liquefaction of starch, or, if necessary the material starch can be first liquefied with acid or  $\alpha$ -amylase to give a relatively low dextrose-equivalent (DE), preferably, DE of lower than 1, then the resultant mixture can be subjected to the action of CGT-ase.

The CGT-ases usable in the invention include microorganisms of the genus Bacillus, for example, those of the species Bacillus stearothermophilus, Bacillus circulans and Bacillus macerans; and those of the genus Klebsiella, for example, those of the species Klebsiella pneumoniae. Particularly, a thermostable CGT-ase specimen derived from a microorganism of the species Bacillus stearothermophilus, which can be used for the gelatinization of starch under heating conditions, can be advantageously used. Furthermore, the starch-debranching enzymes advantageously usable in the invention include pullulanase (EC 3.2.1.41) derived from microorganisms, for example, those of the genus Aerobacter and Bacillus; and isoamylase (EC 3.2.1.68) derived from microorganisms, for example, those of the genus Pseudomonas, Flavobacterium and Cytophaga. These enzymes should not be purified prior to their use as long as they can attain the present object, and, usually supernatants of culture mediums of these microorganisms or their partially purified enzymes are used. Furthermore, the enzymes can be used in an immobilized form, if necessary.

More particularly, the preparation according to the present invention comprises a step of allowing 1-1,000 units/g solid of CGT-ase to act on an aqueous solution containing about 10-50 w/w % of a cyclodextrin or starch at a temperature in the range of about 5-100°C and a pH in the range of 3-9 for an appropriate period of time to form and precipitate amylose granules in the solution. When a starch slurry is used as the material starch, amylose granules are prepared by adding CGT-ase alone or in combination with a starch-debranching enzyme to the starch, heating the mixture at a temperature in the range of 70-100°C to effect gelatinization and liquefaction of the starch, cooling the resultant mixture to a temperature of 60°C or lower, preferably to a temperature in the range of 5-50°C, adding a fresh CGT-ase to the resultant mixture if necessary, and allowing the CGT-ase to act on the resultant mixture for 5-500 hours to form and precipitate amylose granules. The resultant amylose granules can be readily recovered by filtration or centrifugation.

It was found that the amylose granules thus obtained exhibited the following physicochemical properties:

- (1) The amylose granules are approximately globular-shape of amylose granules existing separately or in a conjugation form consisting of two or more of the amylose granules linked together, said amylose granules having about 2-10  $\mu\text{m}$  in diameter or major axis;

- (2) The amylose granules exhibit B type form of starch on powder X-ray diffraction analysis;
- (3) The amylose granules have the number-average molecular weight ( $M_n$ ) of about 4,000-7,000 (average glucose polymerization degree of about 25-43), and the weight-average molecular weight ( $M_w$ ) per the number-average molecular weight ( $M_n$ ) of about 1.4-1.7;
- (4) The color of amylose granules turns blue violet or blue on the iodine coloration; and
- (5) The amylose granules form a theoretical amount of maltose when hydrolyzed by  $\beta$ -amylase.

Furthermore, the amylose granules formed by the action of CGT-ase can be favorably purified by repeating the dissolution and precipitation methods. For example, a white powder of amylose granules is prepared by dissolving crude amylose granules in water by heating, cooling the mixture to precipitate amylose granules, subjecting the resultant mixture to the filtration or centrifugation, and drying the filtrate or the precipitate to obtain a white powder of amylose granules. Furthermore, the powder thus obtained can be favorably pulverized or granulated by conventional methods.

The amylose granules thus obtained have features that those in powder have a satisfiable free-flowing ability, as well as being scarcely hygroscopic, and those dissolved in water by heating are susceptible to the action of an amylase

and readily solidified by cooling.

By using these features, the present amylose granule can be extensively used in the fields of food products, for example, jelly, rice cake, confectionery made of rice, bakery, cookie, confectionery in tablet form, and rice meal; pharmaceuticals, for example, agents in powder-, tablet- or paste-form; and products, for example, mold lubricant, adhesion-preventing agent, filler, and material for film products.

Furthermore, since the present invention can provide a stable preparation of a high-quality amylose granule, such amylose granule can be advantageously used for clinical tests as a substrate for an amylase assay.

The following Experiments will describe the present invention more in detail.

#### Experiment 1

##### Effect of substrate concentration on formation of amylose granules

Aliquots of substrate solution, in which  $\alpha$ -cyclodextrin had been dissolved to give different concentrations, were respectively added with 50 units/g cyclodextrin of a CGT-ase specimen derived from a microorganism of the species Bacillus stearothermophilus, commercialized by Hayashibara Biochemical Laboratories, Inc., Okayama, Japan, and each mixture was allowed to stand at 30°C and at pH 5.5 for 20 hours to form amylose granules which were then recovered by

centrifugation, followed by determining the yield (w/w %). The amylose granules thus obtained were subjected to a gel permeation chromatography using "TSK-GEL G4000PW" and "TSK-GEL G3000PW", both columns were commercialized by Toyo Soda Mfg. Co., Ltd., Tokyo, Japan, and "Shodex STANDARD P-82", commercialized by Showa Denko K.K., Tokyo, Japan, as a molecular standard, to determine the number-average molecular weight ( $M_n$ ). The results were as shown in Table 1.

Table 1

Substrate concentration (w/w %)	Yield (w/w %)	Number-average molecular weight ( $M_n$ )
5	0.0	-
10	14.0	4,800
15	51.0	5,100
20	72.8	5,300
25	84.0	5,300
30	91.7	5,200
35	96.9	5,200

The results in Table 1 showed that the formation of amylose granules depended on the substrate concentration, i.e.

the more the substrate concentration increased, the more the yield of amylose granules increased; and the yield at a substrate concentration of 15 w/w % or higher was 50 w/w % or higher. The amylose granules which had formed at a different substrate concentration had approximately the same level of molecular weight ( $M_n$ ).

### Experiment 2

#### Effect of temperature on formation of amylose granules

A 25 w/w %  $\alpha$ -cyclodextrin solution was added with 50 units/g cyclodextrin of a CGT-ase specimen derived from a microorganism of the species Bacillus stearothermophilus, and the mixture was allowed to stand at pH 5.5 for 20 hours to form amylose granules which were then recovered. The results on the yield and the number-average molecular weight of the amylose granules were shown in Table 2.

Table 2

Temperature (°C)	Yield (w/w %)	Number-average molecular weight (Mn)
12	78.6	4,800
20	86.0	5,200
30	83.5	5,300
40	74.6	6,200
50	56.2	6,200
60	2.6	4,800
70	0.8	3,900

The results in Table 2 showed that the formation of amylose granules depended on the temperature, i.e. the lower the temperature decreased, the more the yield of amylose granules increased; and a temperature of 50°C or lower was favorable for the formation. The molecular weight (Mn) of the amylose granules depended on the temperature.

Experiment 3

Effect of CGT-ase origin on formation of amylose granules

A 25 w/w %  $\alpha$ -cyclodextrin- or  $\gamma$ -cyclodextrin-solution was added with 50 units/g cyclodextrin of a CGT-ase specimen derived from a microorganism of the species Bacillus stearothermophilus or that of Bacillus macerans, and the

mixture was allowed to stand at pH 5.5 and at 40°C for 20 hours to form amylose granules which were then determined on the yield, the number-average molecular weight ( $M_n$ ), and the iodine coloration. The results were as shown in Table 3.

Table 3

Substrate	Origin of CGT-ase specimen	Yield (w/w I)	Number-average molecular weight (Mn)		Iodine coloration $\lambda_{max}$ (nm)
			6,200	5,800	
$\alpha$ -CD	<u>B. stearothermophilus</u>	74.2	6,200	5,800	582.0
	<u>B. macerans</u>	83.4			581.0
$\gamma$ -CD	<u>B. stearothermophilus</u>	73.6	5,700	5,700	572.0
	<u>B. macerans</u>	66.2			562.5

As shown in Table 3, since the yield, the number-average molecular weight, and the iodine coloration of the amylose granules dependently vary on the type of substrate and the origin of CGT-ase, the expected amylose granules can be prepared by using the above variations.

Examples of the present invention will be described hereinafter.

Example 1

An aqueous solution of 25 w/w %  $\alpha$ -cyclodextrin was added with 50 units/g cyclodextrin of a CGT-ase specimen derived from a microorganism of the species Bacillus stearothermophilus, and the mixture was allowed to stand at pH 5.5 and at 30°C for 20 hours to form amylose granules which were then recovered by centrifugation. The amylose granules thus obtained were washed twice with water, and dried at 40°C overnight, followed by recovering the amylose granules in the yield of about 84 w/w %.

The physicochemical properties of the amylose granules were as follows:

(1) Diameter of granule

The scanning electron microscopic analysis ( $\times 2,000$ ) revealed that the amylose granules were approximately globular-shape of amylose granules existing separately or in a conjugation form consisting of two or more of the amylose granules linked together, and that the

amylose granules had about 2-10  $\mu\text{m}$  in diameter or major axis;

(2) Powder X-ray diffraction analysis

The amylose granules and a starch specimen as control were subjected to the powder X-ray diffraction analysis using "GEIGERFLEX RAD-II B (CuK $\alpha$  ray)", an apparatus for X-ray diffraction analysis produced by Rigaku Corp., Tokyo, Japan. The results were as shown in FIG.2. The patterns (1) and (2) in the figure were respectively A and B type forms of starch, while the pattern (3) was the X-ray diffraction pattern of the amylose granules. The analysis revealed that the amylose granules gave the same pattern as that of (2);

(3) Molecular weight

On gel permeation chromatography, the number-average molecular weight ( $M_n$ ) and the weight-average molecular weight ( $M_w$ ) of the amylose granules were determined to give 5,300 and 8,000, respectively. Thus, the ratio of  $M_w/M_n$  is about 1.5 which means that the amylose granules are relatively high-quality of amylose granules with a relatively narrow molecular-weight-distribution;

(4) Specific rotation

$[\alpha]_D^{20} 163^\circ$  ( $l=1$ ,  $c=0.9$ , 0.5N-NaOH);

(5) Infrared absorption spectrum

The KBr tablet method was used and the result was shown in FIG.3;

(6) Iodine coloration

Turning blue with the iodine-iodide solution, and exhibiting  $\lambda_{max}$  around 570mm; and

(7) Hydrolysis by amylase

It is understood that the amylose granules are substantially consisted of  $\alpha$ -1,4 glucosidic linkages because the amylose granules are hydrolyzed by a crystalline  $\beta$ -amylase specimen derived from sweet potato, commercialized by Seikagaku-Kogyo Co., Ltd., Tokyo, Japan, to form a theoretical amount of maltose.

Example 2

An aqueous solution of 25 w/w %  $\gamma$ -cyclodextrin was added with 70 units/g cyclodextrin of a CGT-ase specimen derived from a microorganism of the species Bacillus macerans, and the mixture was allowed to stand at pH 5.7 and at 40°C for 20 hours. Similarly as in Example 1, the amylose granules were washed, dried and recovered in the yield of about 66 w/w %.

The number-average molecular weight (Mn) and the weight-average molecular weight (Mw) of the product were 4,700 and 6,500, and the ratio of Mw/Mn was about 1.4. Furthermore,

the specific rotation of the product was  $[\alpha]_D^{20}$  161°.

The product gave the same physicochemical properties as that of Example 1.

Example 3

A 20 w/w %  $\beta$ -cyclodextrin suspension was added with 200 units/g cyclodextrin of a CGT-ase specimen derived from a microorganism of the species Bacillus stearothermophilus, and the mixture was subjected to an enzymatic reaction for 24 hours in total, i.e. the mixture was first allowed to stand at pH 5.7 and at 50°C for 4 hours, then the resultant mixture was cooled, followed by the successive standing at 40°C for 10 hours and at 30°C for 10 hours. Similarly as in Example 1, the amylose granules were recovered in the yield of about 60 w/w %.

The number-average molecular weight (Mn) and the weight-average molecular weight (Mw) of the product were 5,200 and 7,900, and the ratio of Mw/Mn was about 1.5. Furthermore, the specific rotation of the product was  $[\alpha]_D^{20}$  163°.

The product gave the same physicochemical properties as that of Example 1.

Example 4

A 20 w/w % corn starch slurry, which had been adjusted to pH 6.0, was added with one unit/g solid of a CGT-ase specimen derived from a microorganism of the species Bacillus stearothermophilus, and the mixture was liquefied at 90°C for 20 minutes. The resultant liquefied starch solution was first cooled to 70°C, then added with 5 units/g solid of a

CGT-ase specimen to effect an enzymatic reaction for 24 hours, followed the formation of cyclodextrins. The resultant solution was first kept at 100°C for 20 hours to inactivate the remaining CGT-ase, then adjusted to pH 4.5. The resultant mixture was added with 10 units/g solid of a glucoamylase specimen, and subjected to an enzymatic reaction at 55°C for 20 hours. The resultant solution was first kept at 100°C for 10 minutes to inactivate the remaining glucoamylase, then decolored with an activated charcoal and concentrated.

In accordance with the method disclosed in Japanese Patent Publication No.51,120/87, the concentrated solution was subjected to a column chromatography using a column packed with strongly-acidic cation exchange resins ( $\text{Na}^+$ -form) to remove glucose, followed by the recovery of a mixture of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -cyclodextrins in solution in the yield of about 25 w/w %.

The solution thus obtained was concentrated to give a concentration of about 35 w/w %, and the resultant solution was added with 50 units/g cyclodextrins of a CGT-ase specimen derived from a microorganism of the species of Bacillus stearothermophilus. The mixture was subjected to an enzymatic reaction at pH 5.7 for 24 hours in total, i.e. the mixture was successively incubated at 65°C for 4 hours, at 40°C for 10 hours, and at 30°C for 10 hours. Similarly as in Example 1, the amylose granules were recovered in the yield of about 85 w/w % against the mixture of cyclodextrins.

The number-average molecular weight ( $M_n$ ) and the

weight-average molecular weight (Mw) of the product were 6,600 and 10,500, and the ratio of Mw/Mn was about 1.6. Furthermore, the specific rotation of the product was  $[\alpha]_D^{20}$  166°.

The product gave the same physicochemical properties as that of Example 1.

#### Example 5

A 25 w/w % potato starch slurry, which had been adjusted to pH 6.0, was added with 2 units/g solid of a thermostable CGT-ase specimen derived from a microorganism of the species Bacillus stearothermophilus, and the mixture was liquefied at 90°C for 20 minutes. The liquefied starch solution was first cooled to 55°C, then adjusted to pH 5.5. Thereafter, the resultant mixture was first added with 100 units/g solid of a CGT-ase specimen and 100 units/g solid of an isoamylase specimen, commercialized by Hayashibara Biochemical Laboratories, Inc., Okayama, Japan, then subjected to an enzymatic reaction for 26 hours in total, i.e. the mixture was first incubated at 55°C for 3 hours to form cyclodextrins, then the resultant mixture was successively incubated at 40°C for 6 hours and at 30°C for 17 hours. Similarly as in Example 1, the amylose granules were recovered in the yield of about 55 w/w % against the material starch.

The number-average molecular weight (Mn) and the weight-average molecular weight (Mw) of the product were 5,400 and 9,200, and the ratio of Mw/Mn was about 1.7. Furthermore, the specific rotation of the product was  $[\alpha]_D^{20}$  163°.

The product gave the same physicochemical properties as that of Example 1.

[Effect of the invention]

As described above, the present novel amylose granule is a relatively high-quality of amylose granule having a relatively uniform molecular-weight. Since the amylose granule is formed and precipitated in a reaction solution by allowing cyclodextrin glucanotransferase to act on a cyclodextrin or starch, the separation and recovery of the amylose granule is facilitated without the requirement of a relatively expensive organic-precipitant such as methanol and butanol.

Furthermore, the present invention readily increases the yield of amylose granule to 50 w/w % or higher against the material.

In addition, the present invention is advantageously favorable in that the molecular weight of amylose granule is controllable by varying the source of material starch, origin of CGT-ase, and the conditions such as the concentration and the amount of material starch and CGT-ase.

The amylose granule thus obtained has a free-flowing ability and is scarcely hygroscopic in powder form, while that dissolved in water by heating is susceptibly hydrolyzed by the action of an amylase and readily solidified by cooling. By using these features, the amylose granule according to the present invention can be advantageously used as a material in

the fields of food products, pharmaceuticals and cosmetics. Thus, the present invention has a great significance in these industrial fields.

While there has been described what is at present considered to be the preferred embodiments of the invention, it will be understood that various modifications may be made therein, and it is intended to cover the appended claims all such modifications as fall within the true spirit and scope of the invention.

CLAIMS:

1. An amylose in granule form which exists in an approximately globular-shape of amylose granule or in a conjugation form consisting of two or more of the amylose granules linked together, said amylose granule having about 2-10  $\mu\text{m}$  in diameter or major axis, B type form of starch on powder X-ray diffraction analysis, the number-average molecular weight of about 4,000-7,000 on gel permeation chromatography, and the weight-average molecular weight per the number-average molecular weight of about 1.4-1.7.

2. A process for preparing amylose granule, which comprises:

(a) allowing cyclomaltodextrin glucano-transferase (EC 2.4.1.19) to act on an aqueous solution containing a cyclodextrin or starch to form an amylose granule which is insoluble in said aqueous solution; and

(b) recovering the resultant amylose granule.

3. The process of claim 2, wherein said amylose granule exists in an approximately globular-shape of amylose granule or in a conjugation form consisting of two or more of the amylose granules linked together, said amylose granule having about 2-10  $\mu\text{m}$  in diameter or major axis, B type form of starch on powder X-ray diffraction analysis, the number-average molecular weight of about 4,000-7,000 on gel permeation chromatography, and the weight-average molecular weight per the

number-average molecular weight of about 1.4-1.7.

4. The process of claim 2, wherein said aqueous solution contains about 10-50 w/w % of a cyclodextrin or starch.

5. The process of claim 4, wherein said cyclodextrin is a member selected from the group consisting of  $\alpha$ -cyclodextrin,  $\beta$ -cyclodextrin,  $\gamma$ -cyclodextrin and mixtures thereof.

6. The process of claim 4, wherein said starch is a member selected from the group consisting of potato starch, cane starch, tapioca starch, corn starch, wheat starch, rice starch and mixtures thereof.

7. The process of claim 2, wherein said cyclodextrin (EC 2.4.1.19) is used together with a starch-debranching enzyme.

8. The process of claim 7, wherein said starch-debranching enzyme is a member selected from the group consisting of pullulanase (EC 3.2.1.41), isoamylase (EC 3.2.1.68) and mixtures thereof.

9. The process of claim 2, wherein said cyclomaltodextrin glucanotransferase (EC 2.4.1.19) is used in the range of 1-1,000 units/g solid.

10. The process of claim 2, wherein the temperature in the step (a) is in the range of about 5-100°C.

11. The process of claim 2, wherein the pH in the step (a) is in the range of 3-9.

12. The process of claim 2, wherein the step (c) is effected by filtration or centrifugation.

13. An amylose in granule form substantially as hereinbefore described with reference to any one of the drawings.

14. An amylose in granule form substantially as hereinbefore described with reference to any one of the Examples.

15. A process for preparing amylose granules substantially as hereinbefore described with reference to any one of the Examples.